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(54) **Hair care products comprising an alpha-hydroxy acid and a silicone elastomer**

(57) A hair care products to be washed away after using which contain  $\alpha$ -hydroxycarboxylic acids and water-insoluble silicone elastomer powders.

These hair care products impart softness and smoothness to the moist hair and, after drying, make the hair soft, moist and well styled while keeping smooth or oil-free feel and exerting long-lasting conditioning effects thereon.

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**Description****FIELD OF THE INVENTION**

5 This invention relates to hair care products. More particularly, it relates to hair care products to be washed away after using which can impart softness, smoothness and good combing properties to the moist hair and, after drying, make the hair soft and well styled while keeping smooth feel and exerting long-lasting conditioning effects thereon.

**BACKGROUND OF THE INVENTION**

10 There have been required various hair care products having conditioning effects. In particular, it has been required to develop hair care products capable of imparting softness and smoothness to the moist hair and, after drying, smooth and soft feel and also long-lasting effects thereof to the hair. For example, JP-A-8-34710 proposes a hair care product which contains specific surfactants (anionic/imidazoline type ampholytic surfactants) and an  $\alpha$ -hydroxycarboxylic acid as a conditioning agent (the term "JP-A" as used herein means an "unexamined published Japanese patent application"). However, this product is still unsatisfactory in the effects on the moist hair and smooth feel and long-lasting effects after drying the hair.

15 JP-A-6-80559 discloses a detergent composition which comprises a water-insoluble polymer powder (e.g., a silicone resin) and a water-insoluble, nonvolatile silicone (liquid or paste) dispersed in an aqueous solution of a surfactant. However, this composition fails to impart sufficient softness and moistening effects to the hair.

**SUMMARY OF THE INVENTION**

25 Accordingly, an object of the present invention is to provide hair care products which can impart softness and smoothness to the moist hair and, after drying, exert long-lasting conditioning effects so as to make the hair smooth, soft, moist and well styled.

Under these circumstances, the present inventors have conducted extensive studies. As a result, they have found that the combined use of  $\alpha$ -hydroxycarboxylic acids with specific water-insoluble silicone elastomer powders makes it possible to provide hair care products to be washed away after using which can impart softness and smoothness to the moist hair and, after drying, make the hair soft, moist and well styled while keeping smooth feel and exerting long-lasting conditioning effects thereon, thus completing the present invention.

30 Accordingly, the present invention provides hair care products which comprise  $\alpha$ -hydroxycarboxylic acids and water-insoluble silicone elastomer powders and are to be washed away after using.

**DETAILED DESCRIPTION OF THE INVENTION**

35 The  $\alpha$ -hydroxycarboxylic acids to be used in the present invention comprise mono- or polycarboxylic acids having one or more hydroxyl functional groups at least one of which is introduced into the  $\alpha$ -position (i.e., on the carbon atom adjacent to the carboxyl functional group).

40 Examples of these compounds include citric acid, lactic acid, methylactic acid, phenyllactic acid, malic acid, mandelic acid, glycolic acid, tartronic acid, tartaric acid and gluconic acid. Among these compounds, it is preferable to use citric acid, lactic acid, malic acid, glycolic acid or tartaric acid therefor.

In the present invention, use may be made of either one of these  $\alpha$ -hydroxycarboxylic acids or a combination of two or more of the same. The content of the  $\alpha$ -hydroxycarboxylic acid(s) preferably ranges from 0.01 to 10 % by weight, more preferably from 0.5 to 10 % by weight, based on the whole composition, since the softness of the hair is improved thereby.

50 Examples of the water-insoluble silicone elastomer powders include methylpolysiloxanes, which are obtained by polymerizing or copolymerizing methylhydrogenpolysiloxane, methylvinylpolysiloxane and/or  $\alpha$ - $\omega$ -divinyldimethylpolysiloxane and have rubber elasticity and crosslinked structure, and derivatives thereof. The methylpolysiloxane derivatives are exemplified by amino-modified methylpolysiloxane, phenyl-modified methylpolysiloxane and epoxy-modified methylpolysiloxane. These water-insoluble silicone elastomer powders are called silicone rubber powders which are different from silicone resin powders having a true specific gravity of about 1.3.

55 The water-insoluble silicone elastomer powder may be a composite powder comprising the above-described methylpolysiloxane or derivative thereof as the major component together with other water-insoluble polymer powder(s). Moreover, use may be made therefor of methylpolysiloxane or derivative thereof coated with a water-insoluble polymer by a conventional method. (Hereinafter, they will be sometimes referred to as "composite silicone elastomer powders".) The water-insoluble polymer as used herein includes polymethylsilsesquioxanes; amorphous silicon dioxide; polyethylene, polypropylene, polystyrene, polyamide, polyester or styrene/divinylbenzene copolymers.

The water-insoluble silicone elastomer powder has an average particle size of preferably from 0.01 to 100  $\mu\text{m}$ , more preferably from 0.1 to 30  $\mu\text{m}$ . The particles thereof may have a spherical, oval or spindle shape. Among these, spherical shape is preferable and particularly has a major axis/short axis ratio of 2 or below, preferably 1.3 or below.

It is preferable that the water-insoluble silicone elastomer powder has a true specific gravity of from 0.9 to 1.2, more preferably from 0.9 to 1.1. Further, it is preferable that the water-insoluble silicone elastomer powder has a rubber hardness (determined according to JIS K6253 using Type A Durometer) of from 5 to 95, more preferably from 10 to 90.

Although the water-insoluble silicone elastomer powder may be used as such, it may be employed in the form of a surfactant-containing emulsion having the powder dispersed therein so as to improve the stability and handling properties.

Examples of the water-insoluble silicone elastomer powder include commercially available products such as KMP-598, KMP-597 and X-52-1139G (each manufactured by Shin-Etsu Chemical Co., Ltd.) and Trefil E-500, E-501, E-600, E-602, E-850 and E-730S (each manufactured by Dow Corning Toray Silicone Co., Ltd.).

Use may be made of either one of these water-insoluble silicone elastomer powders or a combination of two or more of the same.

The content of the water-insoluble silicone elastomer powder(s) preferably ranges from 0.01 to 10 % by weight, more preferably from 0.05 to 5 % by weight, based on the whole composition, since the smoothness and combing properties of the moist hair and the smooth feel and the persistence of the conditioning effects after drying the hair is improved - thereby.

The hair care product of the present invention may further contain surfactant(s). These surfactants are not particularly restricted but arbitrarily selected from those commonly employed in cosmetics.

To produce shampoo compositions, use can be made of one or more surfactants selected from anionic, ampholytic and nonionic surfactants as the major component optionally together with cationic surfactant. The content of the surfactant(s) in the composition preferably ranges from 5 to 30 % by weight, in particular, 10 to 25 % by weight, based on the whole composition.

To produce rinses or hair conditioners, use can be made of one or more surfactants selected from cationic and non-ionic surfactants as the major component optionally together with ampholytic and anionic surfactants. The content of the surfactant(s) in the composition preferably ranges from 0.1 to 20 % by weight, in particular, 0.5 to 10 % by weight, based on the whole composition.

In addition to the components described above, the hair care products of the present invention may optionally contain components commonly employed in cosmetics, such as oily components such as hydrocarbon oils, vegetable oils, fatty acids, ester oils, perfluoropolyethers and silicone derivatives; medicinal components such as antidandruff agents, bactericides and vitamins; preservatives such as paraben; thickeners such as water-soluble polymers; coloring matters such as dyes and pigments; conditioning agents such as cationic polymers; pearling agents such as glycol esters; and those listed in *ENCYCLOPEDIA OF CONDITIONING RINSE INGREDIENTS* (MICELLE PRESS, 1987), so long as the effects of the present invention are not deteriorated thereby.

The hair care products of the present invention can be produced by blending the components in a conventional manner. The hair care products of the present invention may be in the form of products to be washed away after using, for example, shampoo compositions such as shampoos and rinse-in-shampoos, rinses, hair treatments, hair conditioners and hair packs.

#### EFFECTS OF THE INVENTION

The hair care products of the present invention can impart softness, smoothness and good combing properties to the moist hair and, after drying, make the hair soft, moist and well styled while keeping smooth or oil-free feel and exerting long-lasting conditioning effects thereon.

#### [Examples]

To further illustrate the present invention in greater detail, and not by way of limitation, the following Examples will be given.

#### Example 1

A shampoo composition as shown in Table 1 was produced in the conventional manner. After using it, evaluation was made on the softness and slipperiness of the moist hair, the softness, moist feel, smooth feel and slipperiness of the hair after drying and the persistence of the conditioning effects. The results are shown in Table 1.

(Evaluation method)

(1) Textures of moist hair and dry hair

5        2 g of the shampoo was applied onto a human tress (weight: about 25 g, length: about 20 cm). After foaming the shampoo for 1 minutes, the tress was rinsed with running water for 30 seconds and then towel-dried. Then the texture of the moist hair and that of the hair dried with a dryer were organoleptically evaluated by skilled panelists in accordance with the following criteria.

- 10    E:    excellent.  
       G:    good.  
       M:    moderate.  
       B:    bad.

15    (2) Persistence of conditioning effect

      The hair was shampooed, rinsed and towel-dried in the conventional manner and then the persistence of the conditioning effects (expressed in the change in the texture of the hair after 24 hours) was organoleptically evaluated by skilled panelists in accordance with the following criteria.

- 20    E:    excellent; long-lasting effects.  
       G:    good; lasting effects.  
       M:    moderate.  
       B:    bad; non-lasting effects.

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Table 1

Component (wt. %)	Invention product				Comparative product			
	1	2	3	4	1	2	3	4
(1) Sodium polyoxyethylene lauryl ether sulfate (EO = 3)	16.0	16.0	16.0	16.0	16.0	16.0	16.0	16.0
(2) Coconut fatty acid diethanolamide	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
(3) Lauric acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
(4) Ethanol	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
(5) Lactic acid	1.0	2.0	2.0	3.0	2.0	-	-	2.0
(6) Silicone elastomer powder (KMP-597, mfd. by Shin-Etsu Chemical Co., Ltd., av. particle size: 5 $\mu$ m, true specific gravity: 0.97)	0.5	-	1.0	2.0	-	1.0	-	-
(7) Silicone elastomer composite powder (X-52-1139G, mfd. by Shin-Etsu Chemical Industry Co., Ltd., av. particle size: 12 $\mu$ m, true specific gravity: 0.97)	-	0.3	0.2	-	-	-	-	-
(8) Silicone resin composite powder (Tospearl 130, mfd. by Toshiba Silicone Co., Ltd., av. particle size: 3 $\mu$ m, true specific gravity: 1.32)	-	-	-	-	-	-	1.0	0.5
(9) Cationized cellulose (Cathinal LC-100, mfd. by Toho Chemical Industry Co., Ltd.)	0.5	0.5	-	0.5	-	0.5	-	0.5
(10) High-polymerization methylpolysiloxane (15x10 <sup>6</sup> cs)	1.5	1.5	1.5	-	1.5	-	1.5	-
(11) Dimethylpolysiloxane (200 cs)	1.5	1.5	1.5	-	1.5	-	1.5	-
(12) Preservative, Colorant, Perfume	s.q. bal.	s.q. bal.	s.q. bal.	s.q. bal.	s.q. bal.	s.q. bal.	s.q. bal.	s.q. bal.
(13) Purified water								

Table 1 (cont'd)

Component (wt. %)	Invention product				Comparative product			
	1	2	3	4	1	2	3	4
Conditioning effects								
moist hair: softness	E	E	E	E	G	M	M	M
slipperiness	E	E	E	E	M	G	G	G
dry hair: softness	E	E	E	E	G	M	M	M
moist feel	E	E	E	E	M	B	B	M
oil-free feel	E	E	E	E	M	G	G	G
slipperiness	E	E	E	E	M	M	G	G
persistence of conditioning effect	E	E	E	E	B	G	M	M

S.q.: sufficient quantity  
bal : balance

Example 2 (Shampoo)

A shampoo having the following composition was produced in the conventional manner.

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(Component)		(wt%)
(1)	Sodium polyoxyethylene lauryl ether sulfate (EO = 3)	15.0
10 (2)	Coconut fatty acid diethanolamide	3.0
(3)	Amidopropylbetaine laurate	2.0
(4)	Ethylene glycol distearate	3.0
15 (5)	Glycolic acid	2.5
(6)	Silicone elastomer powder (Trefil E-500, mfd. by Dow Corning Toray Silicone Co., Ltd., average particle size: 3 $\mu$ m, true specific gravity: 0.97)	1.0
(7)	Cationic polymer (Merquat 550, mfd. by Calgon Corporation)	0.3
20 (8)	High polymerization methylpolysiloxane ( $6 \times 10^6$ cs)	2.0
(9)	Dimethylpolysiloxane (200 cs)	1.5
(10)	Ethanol	2.0
(11)	Preservative, Colorant, Perfume	sufficient quantity
25 (12)	Purified water	balance

Example 3 (Shampoo)

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A shampoo having the following composition was produced in the conventional manner.

(Component)		(wt%)
35 (1)	Ammonium lauryl sulfate	17.0
(2)	Coconut fatty acid diethanolamide	2.0
(3)	Amidoamino acid triethanolamine	2.0
40 (4)	Ethylene glycol distearate	3.0
(5)	Lactic acid	1.5
(6)	Citric acid	1.0
45 (7)	Silicone elastomer powder (Trefil E-501, mfd. by Dow Corning Toray Silicone Co., Ltd., average particle size: 10 $\mu$ m, true specific gravity: 0.97)	1.0
(8)	Cationic polymer (Polymer JR-400, mfd. by Union Carbide Co., Ltd.)	0.2
(9)	Stearyltrimethylammonium chloride	0.1
50 (10)	High polymerization methylpolysiloxane ( $1 \times 10^7$ cs)	1.8
(11)	Dimethylpolysiloxane (200 cs)	1.5
(12)	Ethanol	2.0
(13)	Preservative, Colorant, Perfume	sufficient quantity
55 (14)	Purified water	balance

**Example 4 (Hair conditioner)**

A hair conditioner of the following composition was produced in the conventional manner.

(Component)	(wt%)
(1) Cetostearyltrimethylammonium chloride	2.0
(2) Cetanol	2.5
(3) Isopropyl palmitate	1.0
(4) Purified lanolin	0.5
(5) Lactic acid	1.5
(6) Silicone elastomer powder (Trefil E-500, mfd. by Dow Corning Toray Silicone Co., Ltd., average particle size: 3 $\mu$ m, true specific gravity: 0.97)	1.0
(7) Hydroxyethyl cellulose	0.5
(8) High polymerization methylpolysiloxane ( $6 \times 10^6$ cs)	0.5
(9) Dimethylpolysiloxane (200 cs)	0.3
(10) Preservative, Colorant, Perfume	sufficient quantity
(11) Purified water	balance

The hair care products obtained in the above Examples 2 to 4 each imparted softness and smoothness to the moist hair and, after drying, made the hair soft, moist and well styled while keeping smooth or oil-free feel and exerting long-lasting conditioning effects thereon.

**Claims**

1. A hair care product which comprises an  $\alpha$ -hydroxycarboxylic acid and a water-insoluble silicone elastomer powder and is to be washed away after using.
2. The hair care product as claimed in Claim 1, wherein said  $\alpha$ -hydroxycarboxylic acid is at least one acid selected from citric acid, lactic acid, malic acid, glycolic acid and tartaric acid.
3. The hair care product as claimed in Claim 1 or 2, wherein said  $\alpha$ -hydroxycarboxylic acid is contained in an amount of from 0.01 to 10 % by weight.
4. The hair care product as claimed in any of Claims 1 to 3, wherein said water-insoluble silicone elastomer powder has an average particle size of from 0.01 to 100  $\mu$ m.
5. The hair care product as claimed in any of Claims 1 to 4, wherein said water-insoluble silicone elastomer powder is contained in an amount of from 0.01 to 10 % by weight.
6. The hair care product as claimed in any of Claims 1 to 5, wherein said water-insoluble silicone elastomer powder has a true specific gravity of from 0.9 to 1.2.
7. The hair care product as claimed in any of Claims 1 to 6, wherein said water-insoluble silicone elastomer powder has a spherical shape.
8. Use of a hair care product which contains an  $\alpha$ -hydroxycarboxylic acid and a water-insoluble silicone elastomer powder as a shampoo.
9. Use of a hair care product which contains an  $\alpha$ -hydroxycarboxylic acid and a water-insoluble silicone elastomer powder as a rinse or a hair conditioner.





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**ANNEX TO THE EUROPEAN SEARCH REPORT  
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
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